Modulating the Surface Environment of Lead Sulfide Quantum Dots to Manipulate Energy Transfer across the Inorganic–organic Interface

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Abstract

Elucidating the mechanism behind energy transport is essential to improving the efficiency of energy related functions. In our project, we attempt to uncover the nature of energy transfer dynamics between lead sulfide quantum dots (PbS QDs) and surface bound perylene diimide (PDI) molecules. The two species are energetically aligned in such a way that energy can transfer between them even though they absorb in different regions of the light spectrum. Using transient absorption spectroscopy, we selectively excited the PbS QDs and observed how the system relaxes on a femtosecond timescale. We found that PbS QD transfers an excited electron to PDI within 30 picoseconds to create a radical PDI anion. Furthermore, we can make this process faster or slower by adding cinnamate molecules to the QD surface, which serve to move the energy levels of PbS QDs up and down. This means that we can change the energetic alignment between PbS QD and PDI by synthetically modifying the surface's electronic environment. This realization is significant because it adds an additional degree of control to preparing energy devices. We believe that this will help in guiding future designs to engineer light harvesting materials.

Background

Over the years, innovative techniques have pushed the boundaries of what we can achieve in terms of harvesting energy in environmentally friendly ways. Finding methods to generate usable energy from the sun's light rays is a huge field in many areas of science. Using light to perform any function – such as photosynthesis or electricity generation – relies on two general processes: 1) the conversion of photons into excited energy carriers and 2) the transport of those energy carriers into a species that can harness the energy to perform that function. As such, there is a large focus on uncovering the fundamental science behind energy transport, especially in materials that can absorb light well.

Organic semiconductors, one type of those materials, have unique properties that make them desirable in the field of energy. Through a process called singlet fission (SF), they can turn a single photon into two long-lived, lower energy excited states that would normally take two photons to generate in other materials. This is made possible by manipulation of electron spin as well as energy transfer between neighboring molecules. Organic semiconductors can also do the reverse process to turn two lower energy excited states back into the higher energy state through a process called triplet fusion (TF). In general, the lower energy excited states in an organic molecule are called triplet excited states, and the higher energy excited state is called a singlet excited state.

The ability to create additional excited states (in the case of SF) or access a higher energy from low energy photons (in the case of TF) is incredible and provides new ways to convert light into function. One potential drawback, however, is that organic semiconductors are unable to directly turn light into low energy triplet excited states due to quantum rules on the nature of electron spin. As a solution to this problem, Bender *et al.* showed that inorganic semiconductor nanocrystals, otherwise known as quantum dots (QDs), can anchor organic semiconductors on their surface and transfer triplet excited states into the bound molecules[1].

Quantum dots are also really interesting materials because their photophysical properties are dictated by quantum mechanical phenomena: the energy of light that they absorb, otherwise known as their optical band gap, changes as the size of the QD is varied. Therefore, these materials can be synthetically tuned to span a large spectral range of wavelengths, making them useful for many different applications. Furthermore, QDs are protected by a layer of insulating organic ligands that ensure chemical stability of their positively charged surface. These native organic ligands, usually oleate molecules, can be exchanged for any other organic molecule that contains a negatively charged binding group; this makes anchoring organic semiconductors on a QD surface possible. Generally, inorganic materials can access triplet excited states more readily than organic materials because spin is not as highly conserved. However, inorganic materials do not possess the special properties that organic molecules show, which makes pairing the two types of materials a powerful combination.

As it turns out, these hybrid inorganic–organic QD systems can be used for a variety of applications. Hammer *et al.* showed that oligo-(phenylene vinylene) molecules bound to cadmium sulfide QDs can enhance energy transfer and spectral stability[2]. More recently, Xia *et al.* demonstrated that anthracene molecules bound to silicon QDs can facilitate photon upconversion, a process by which low energy photons are converted to high energy photons[3]. Studying energy transfer across the inorganic–organic interface in these hybrid QD systems is a rich field in physical chemistry that can potentially lead to a heap of new applications.

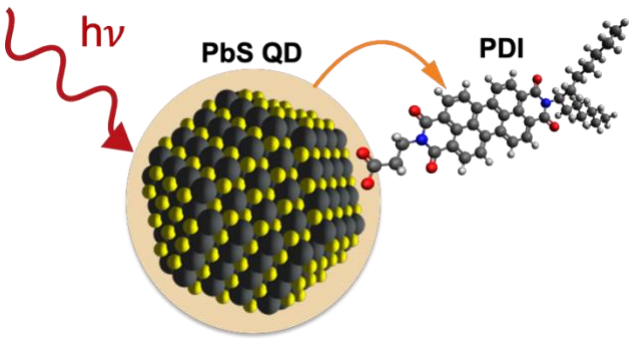

Figure 1: Diagram of our chemical system. Low energy light excites the PbS QD, causing energy transfer to the PDI molecule.

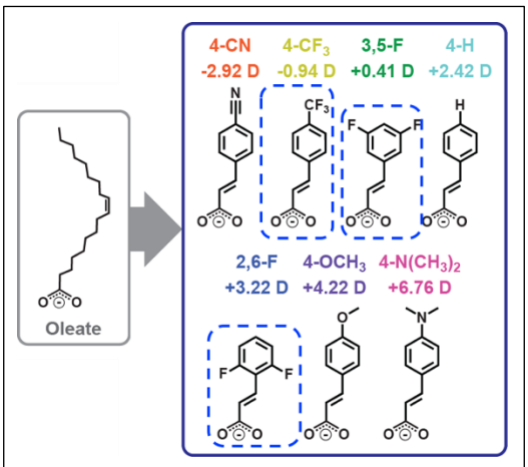

Figure 2: Native oleate ligands can be exchanged for cinnamate molecules that have a permanent dipole moment. The molecules that were used in this study are circled in blue.

Thus, we have chosen to investigate perylene diimide (PDI) molecules bound to the surface of lead sulfide (PbS) QDs. PDI molecules were chosen for two reasons: they are amazingly stable in the presence of light and oxygen (which is relatively rare for organic semiconductors), and we can change the structure of these molecules at their tail ends without significantly changing their core electronic properties. The second point is particularly useful because we can add a binding functional group on one end. We chose to pair these PDIs with PbS QDs because of their favorable energetic alignment, making it likely for interactions such as energy transfer to occur. At the same time, PbS QDs absorb in the infrared region while PDIs absorb in the visible region. By shining infrared light on this system, we can selectively excite the PbS QDs and observe the system's subsequent relaxation dynamics. In this project, we seek to observe 1) whether PbS QDs can transfer

energy to PDI molecules, 2) what kind of excited states form on the PDI as a result, and 3) how fast this process occurs.

On a separate note, there is an interesting interaction that occurs when a class of organic molecules called cinnamates, shown in Figure 2, are added to the surface of PbS QDs. These cinnamate molecules each have an associated permanent dipole moment, which is when charge is unevenly distributed throughout the molecule. Adding these molecules severely changes the electronic nature at the PbS QD surface, altering the local environment[4]. This causes the valence band and conduction band of the PbS QDs to shift up or down in energy; the extent and direction of the shift can be related to the magnitude of the cinnamate's permanent dipole moment. As you will see later, this quality will be extremely useful for our application in this investigation.

Finally, the experiment we use to monitor the dynamics of the system's excited state is called transient absorption (TA) spectroscopy. This technique can monitor how the sample's absorption changes over time as it is photoexcited and relaxes back down to its ground state. Energy relaxation occurs at ultrafast timescales, and observing it requires the use of an ultrafast laser that can send extremely short pulses of light. In a TA experiment, a probe pulse is first sent through the sample to detect the ground state absorption and generate a "pump-off" signal; this is analogous to taking a UV-Vis absorption spectrum. Then, a monochromatic pump pulse is used to excite the sample. We can probe the excited state system's new absorption features at a time delay, Δt, after the pump pulse to generate a "pump-on" signal. The resulting signal is represented as ΔAbsorption and is obtained by subtracting the "pump-off" signal from the "pump-on" signal. We can observe this signal for many time delays to track how the system's dynamics, represented by ΔA, change as a function of time and probe wavelength.

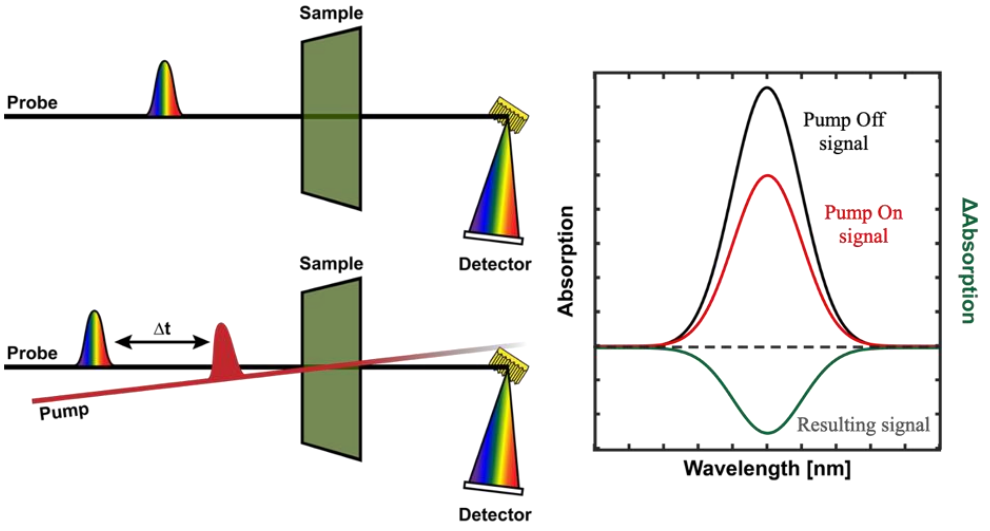

Figure 3: Diagram of how signals in transient absorption spectroscopy are generated.

Results

The first goal for our project was to create a reliable and reproducible procedure for synthesizing PbS quantum dots. Initially, we used the procedure from Weidman *et al.* that involved combining lead (II) chloride with elemental sulfur to produce PbS quantum dots that were surface passivated with chloride ions[5]. However, we eventually learned that energy transfer to organic ligands was not possible with these quantum dots since there was no change in excited state dynamics between PbS/oleate and PbS/PDI. Most likely, the chloride ions on the surface were forming an insulating barrier that prevents energy transfer.

We shifted our attention to a different PbS synthetic procedure from Hines and Scholes that involved combining lead oxide with bis(trimethylsilyl)sulfide (TMS)[6]. This procedure produced clean PbS quantum dots that were monodisperse in size. Absorption spectroscopy was the main tool for characterizing the success of each synthesis; a distinct 1st exciton absorption peak was taken as a signal that the synthesis went well. Figure 4 shows an example of a successful PbS quantum dot synthesis with a distinct 1st exciton peak centered at 1340 nm.

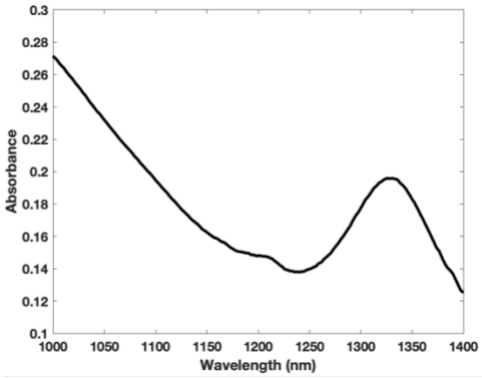

Figure 4: Absorption spectrum of successfully synthesized PbS QD batch.

However, we wanted to achieve ultra-small quantum dots that could absorb 1000 nm wavelength light, or 1.24 eV. Up to this point, the quantum dot batches that were made could only absorb 1200 to 1400 nm light, and getting them even smaller in size was a huge struggle. Eventually, with the help of a modified procedure from Kessler *et al.* that routinely obtained PbS quantum dots that could absorb 800 nm light, we found that the key to achieving small quantum dots was the molar ratio of oleic acid (capping ligand) to lead oxide[7]. We found that if the number of capping ligands, which serve to stabilize the surface of quantum dots during their growth, is limited in the reaction, the size of the quantum dots is also limited. This crucial piece of information along with maintaining excellent control over the temperature of the reaction helped us to control the size of our quantum dots and their absorption energy more consistently.

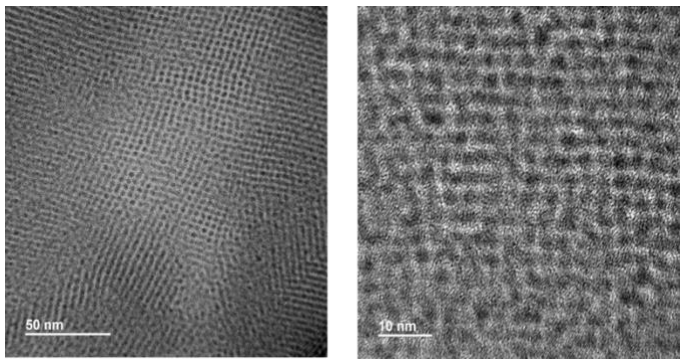

Figure 5: TEM images of PbS QDs, taken with **a)** 50 nm resolution and **b)** 10 nm resolution. Scale bars are shown in the bottom left.

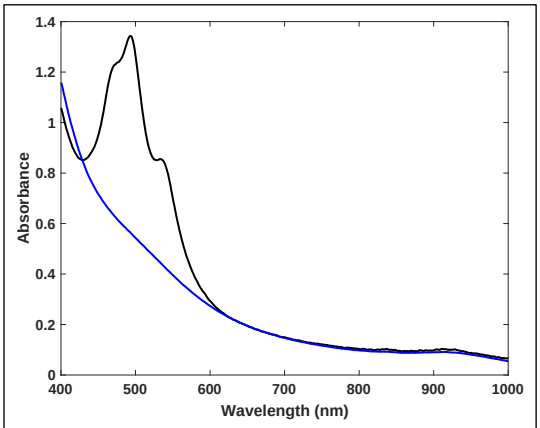

Figure 6: Absorption spectrum of regular PbS QDs (blue) vs PDI-functionalized PbS QDs (black).

The next step in the project was to obtain a consistent procedure for exchanging the native oleate ligands on the surface for PDI molecules. These PDI molecules were asymmetrically functionalized to provide both surface binding capability and solubility. Previously, we had studied they dynamics of triplet energy transfer from PbS quantum dots to TIPS-pentacene ligands, so we used the procedure for exchanging TIPS-pentacene onto the surface as a starting point[1]. There are two main methods for ligand exchange: 1) the quantum dots and ligands are stirred together in a common solvent, washed, and redispersed, or 2) the quantum dots are spun down into a film and exposed to a solution of solvated ligands for a long period of time. To create PDI-functionalized PbS quantum dots, we found that method 1 is the preferred method of ligand exchange. Absorption spectroscopy was used to characterize the binding of PDI to PbS QDs; as shown in Figure 6, PbS QDs showed new absorption features in the visible region after PDIs were exchanged onto the surface. Furthermore, the absorption lineshape of bound PDIs is significantly different than that of PDIs freely moving in solution. This will be discussed further later on.

Figures 7a and 7b show the transient absorption spectra of PbS quantum dots with native oleate ligands and PDI-functionalized PbS quantum dots in a side-by-side comparison. The samples were both excited with a pump wavelength of 800 nm and probed in the visible region with femtosecond time resolution. The large, long-lived, positive ΔA signal (called induced absorption) in 7a is characteristic of PbS quantum dots; when an electron is promoted to the conduction band, new intra-conduction band excitations are possible, causing the excited PbS QDs to absorb more strongly in this spectral region. There is a big difference in the system's spectral features when PDI molecules are introduced to the surface. At later time points, a new negative ΔA feature shows up blue of 500 nm, which is right where the PDI molecules absorb. We attribute this to the bleaching of the PDI molecules: when a HOMO-LUMO excitation is induced in the PDI, less electrons are available for the same transition, causing the absorption of the excited state to decrease. With this information, we can definitively conclude that we are transferring energy of some sort from the PbS QD to the PDI, further corroborating that the PDI molecules are indeed on the surface.

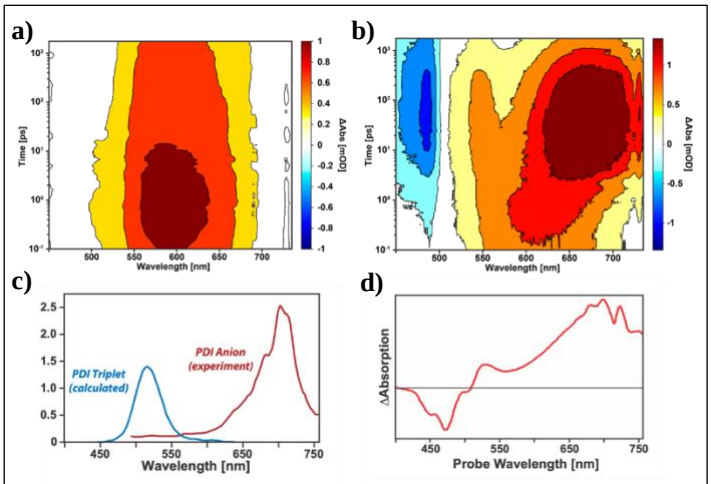

Figure 7: a) TA spectrum of PbS QDs without PDI. **b)** TA spectrum of PDI-functionalized PbS QDs. **c)** Absorption lineshape of PDI triplet and PDI anion. **d)** Spectral trace taken from (b) at long times.

At the same time, the induced absorption signal shifts to lower energy and becomes more intense. The fact that this occurs at the same time as the PDI bleaching indicates that these two signals stem from a single energy transfer process. Figure 7c shows the absorption lineshape of a PDI triplet and a PDI anion taken from Hedström *et al.*, and Figure 7d shows a spectral trace that was taken from 7b at long times[8]. As you can see, the induced absorption signal is similar to the PDI anion absorption lineshape in the way it peaks and broadens. Based on these observations, we concluded that the PbS QD transferred an excited electron to the PDI molecule, leaving behind a PDI anion.

An energy diagram representing this transition is illustrated in Figure 8. Due to energetic alignment between the conduction band of a PbS QD and the LUMO of PDI, it is thermodynamically favorable for an excited conduction band electron to transfer to the PDI LUMO – provided that the PbS and PDI are close enough to interact. It follows logically that moving the bands of PbS QD up and down in energy might change the physical properties of this process. We hypothesized that if we could move the conduction band closer or further away in energy from the LUMO orbital via the addition of cinnamate molecules, thereby altering the thermodynamic properties of the electron transfer process, we could change the system's energy transfer kinetics – based on Marcus theory.

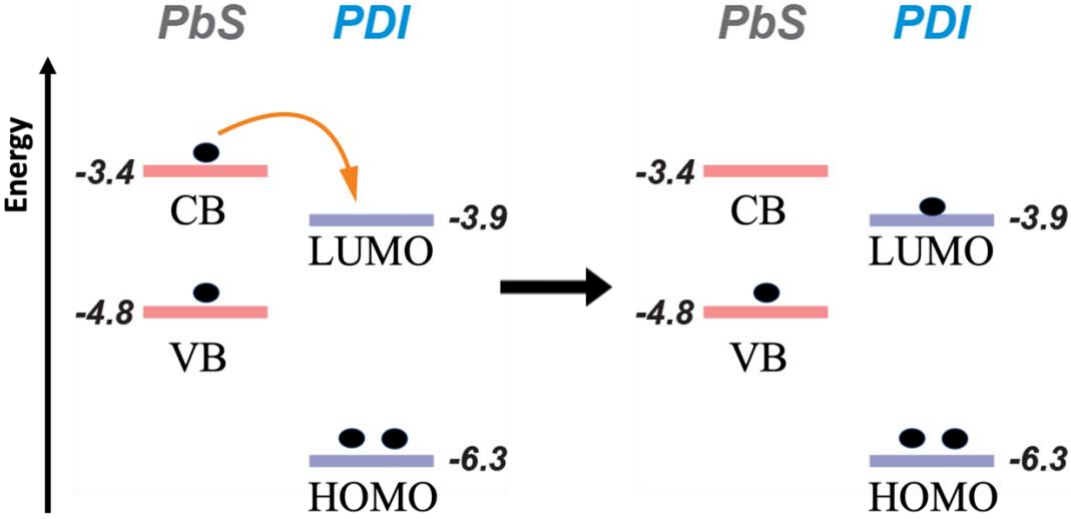

Figure 8: Schematic of electron transfer process in PDI-functionalized PbS QDs.

We chose to investigate three of the cinnamate molecules shown in Figure 2. 3,5-difluorocinnamate (3,5-F-CA) and 4-trifluoromethylcinnamate (4-CF_3-CA) shift the PbS QD bands down in energy, and 2,6-difluorocinnamate (2,6-F-CA) shifts the PbS QD bands up in energy. Exchanging these cinnamate molecules onto the surface of PbS quantum dots was routine, given that the procedure is well documented by Kroupa *et al*[4]. The ligand exchanges were characterized by ^{1}H NMR, ^{19}F NMR, and FTIR, as shown in Figure 9. Figure 9a shows a ^{1}H NMR spectrum with a broad peak at about 6.02 ppm that is characteristic of surface bound oleate molecules; this peak disappears when cinnamates are exchanged onto the surface, as shown in 9b[9]. Figure 9c shows a ^{19}F NMR spectrum with a relatively broad peak at -109.85 ppm, which is characteristic of surface bound, fluorinated cinnamate molecules[10]. In both proton and fluorine

NMR, unbound ligands will show up as a much sharper peak; thus, NMR can be used to quantify the ratio between unbound and bound ligands in the sample. Figure 9d shows an FTIR spectrum of PbS QDs with each ligand environment. As you can see, the oleate trace (black) is completely different from the other samples. The peaks that show up between 2800 and 3000 cm^{-1} can be assigned to C–H stretching vibrations in oleate molecules. In the three cinnamate traces, these peaks significantly decrease in intensity. These three techniques provide significant evidence that the cinnamate exchanges were successful.

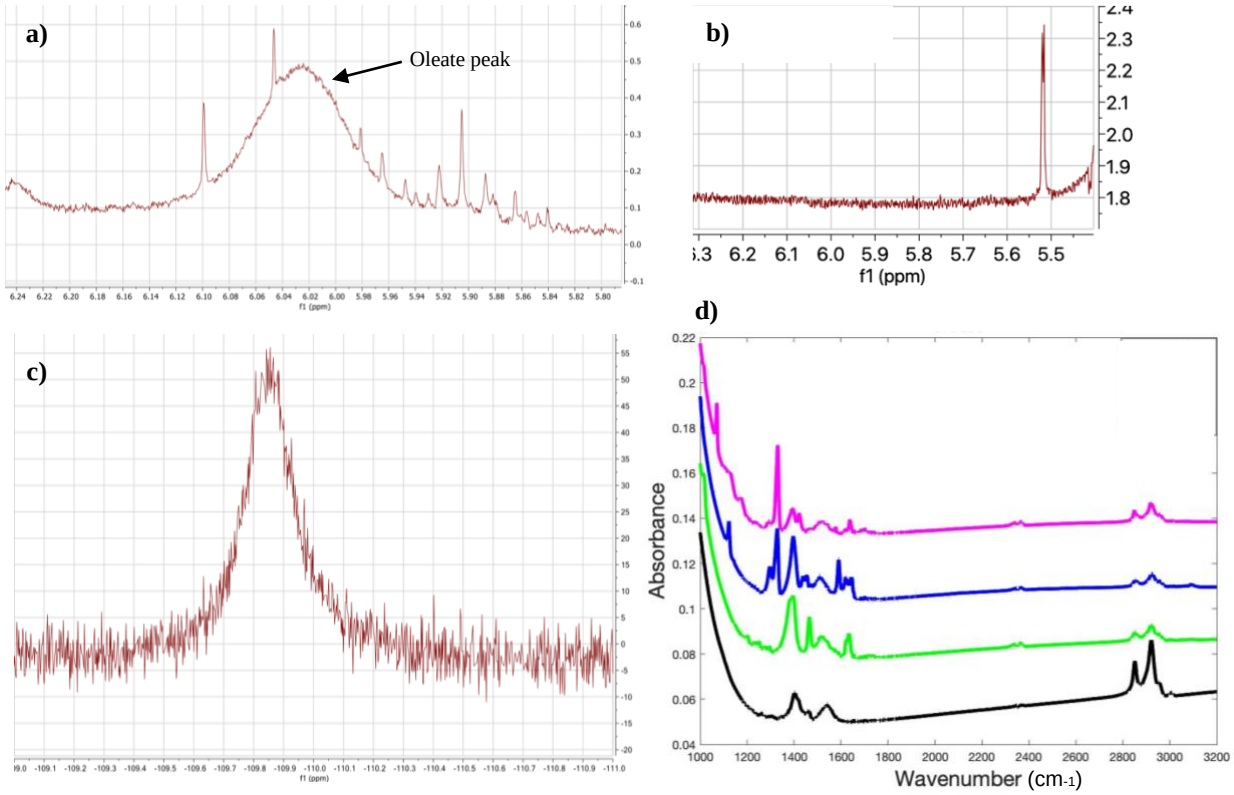

Figure 9: a) ^{1}H NMR spectrum of PbS QDs with native oleate ligands. **b)** 19F NMR spectrum of PbS with 2,6-F-CA ligands. There is no unbound signal in this spectrum. **c)** FTIR spectrum of PbS QDs with surface environment of oleates (black), 2,6-F-CA (green), 3,5-F-CA (blue), and 4-CF_3-CA (pink).

After modifying their surface environment, the PbS QDs were functionalized with PDI molecules, and transient absorption experiments were performed. Figure 10 displays the transient absorption spectra for each PbS surface environment, ordered as a function of the relative shift in PbS band energy. You can see that there is a noticeable difference in the onset of the PDI anion's spectral features; electron transfer kinetics are definitely changing as the PbS surface environment is altered. Data calculations showed that the electron transfer rate slowed down as the conduction band moved lower in energy; conversely, electron transfer became faster when the conduction band was moved higher in energy. The time it takes for electron transfer to occur is represented by $\tau_{ET,intrinsic}$.

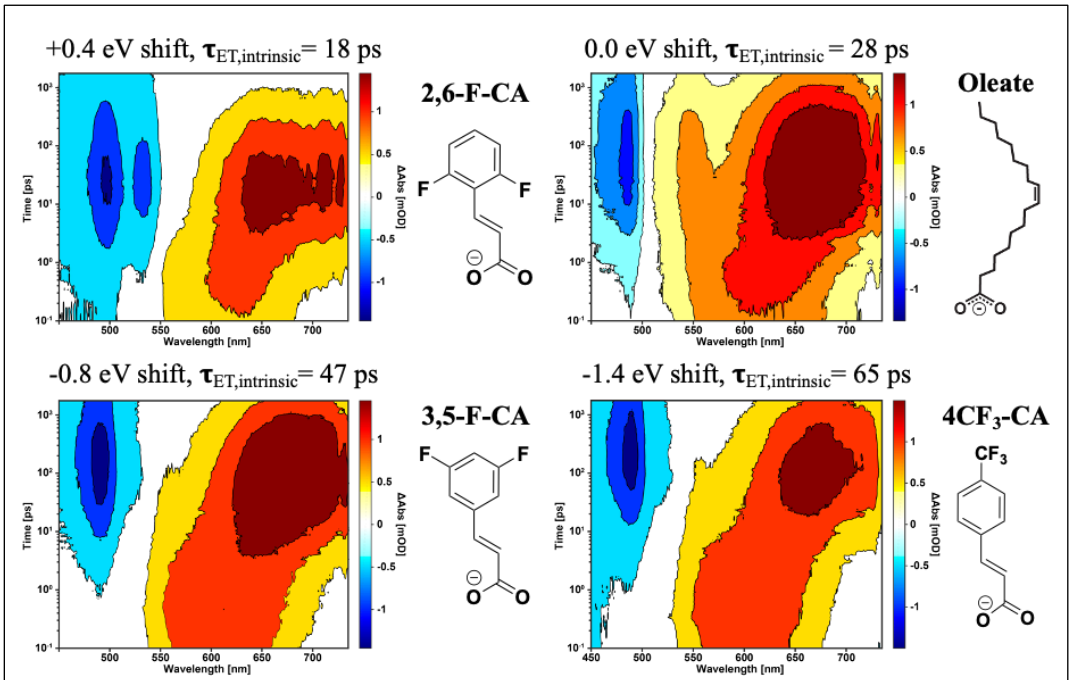

Figure 10: Transient absorption spectrum, relative eV shift, and time it takes for electron transfer to occur for PDI-functionalized PbS QDs with **a)** 2,6-F-CA, **b)** native oleate, **c)** 3,5-F-CA , and **d)** 4-CF_3-CA ligands.

Table 1: Comparison of the average number of PDI molecules on on PbS QD and the time it takes for electron transfer to occur for two different ligand environments. $\tau_{ET,intrinsic}$ is normalized for number of PDIs.

4-CF_3-CA			
$\langle N_{PDI} \rangle$	3.3	2.4	0.7
$\tau_{ET,\ observed}$ (ps)	20	26	32
$\tau_{ET,\ intrinsic}$ (ps)	65	60	21
Oleate			
$\langle N_{PDI} \rangle$	5.7	2.1	0.6
$\tau_{ET,\ observed}$ (ps)	5	13	22
$\tau_{ET,\ intrinsic}$ (ps)	28	27	13

It is important to mention that the steady state absorption lineshape of PbS QDs does not change with the addition of cinnamate molecules; however, the absorption lineshape of the bound PDIs does change depending on which cinnamate molecule is added. Changes to the vibronic structure of the absorption lineshape is usually taken to mean that PDI molecules are aggregating together, which causes interactions that alter the PDIs' core electronic structure. This suggests that PDI molecules are preferentially binding to sites that are near other PDI molecules. To investigate the impact of this on electron transfer, we performed the same TA experiments to extract the electron transfer rates on a series of samples that differed in the number of bound PDI molecules. The results are shown for two different ligand environments in Table 1. It is clear that the electron transfer rate is changing as we modify the amount of PDIs on the surface. If we normalize the time it takes for electron transfer to occur by the estimated number of PDI molecules, you can see that $\tau_{ET,intrinsic}$ significantly goes down near the limit of ~0.5 PDIs per QD. This suggests that electron transfer is fastest when we approach the limit where every PDI molecule is isolated, far away from other PDI molecules.

Discussion and Conclusions

Acquiring a consistent synthetic procedure for making PbS QDs proved to be very useful because it gives us the ability to tinker with their surface environment as well as their energetic properties. However, it remains to be seen how changing the size and energy of the QDs impacts energy transfer across the inorganic–organic interface. Their size tunability gives us an additional dimension of control to explore for manipulating the system's thermodynamic and kinetic properties.

One part that doesn't quite make sense in the data is that the time it takes for electron transfer to occur is not changing very drastically in comparison to the huge band shifts on the eV scale that were occurring due to cinnamate. These band shift values were taken from Kroupa *et al.*, where they made their band measurements on solid-state PbS QDs[4]. Energy shifts of that magnitude could only arise with severe changes to the electronic environment on the surface. We think that the band shifts in our system are not quite as large because our samples are in solution, since the solvent can stabilize charge on the surface of the QDs. An interesting experiment to conduct in the future would be to investigate how electron transfer rates change when the system is spun into a solid-state film, getting rid of the solvation layer around the QDs. Causing the QDs to pack closely together may have implications on both the surface environment as well as PDI aggregation behavior.

It is also possible that the electronic structure of the PDIs is being influenced by the positively charged surface of the PbS QDs. An interaction between the core of the PDI and Pb^{2+} on the surface could potentially cause changes to the absorption lineshape. Preliminary theoretical calculations suggest that there is indeed some degree of interaction between PDI's core and the surface. However, the data in Table 1 is strong evidence that PDI aggregation plays a large factor in this system. Research on the nature of the binding interaction when PDI is exchanged onto the surface and how that changes due to the surface environment is crucial to understanding the system's properties.

Finally, the fact that excitation of the PbS QDs leads to negatively charged PDI anions on the surface carries exciting and new applications. These anionic molecules contain an extra radical electron that render them highly reactive and unstable; thus, we believe this kind of process could be used for catalyzing chemical reactions. This is efficient from an energy standpoint because the excitation of PbS QDs only requires low energy, near-infrared light. Furthermore, we can tune the thermodynamic and kinetic properties of this electron transfer process, which indicates that we have a certain degree of control over the system's behavior. We have reason to believe that PbS QDs have the potential to transfer energy to PDIs in the form of triplet excited states if we make electron transfer highly thermodynamically unfavorable. This concept is a really unique and exciting avenue, given that we would be able to tune which energy transfer process occurs – expanding the range of this system's potential applications – all by synthetically modifying the QD surface environment.

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References

(1) Bender, J. A.; Raulerson, E. K.; Li, X.; Goldzak, T.; Xia, P.; Van Voorhis, T.; Tang, M. L.; Roberts, S. T. Surface States Mediate Triplet Energy Transfer in Nanocrystal–Acene Composite Systems. *Journal of the American Chemical Society* **2018**, *140* (24), 7543–7553. https://doi.org/10.1021/jacs.8b01966.

(2) Hammer, N. I.; Emrick, T.; Barnes, M. D. Quantum Dots Coordinated with Conjugated Organic Ligands: New Nanomaterials with Novel Photophysics. *Nanoscale Res Lett* **2007**, *2* (6), 282–290. https://doi.org/10.1007/s11671-007-9062-8.

(3) Xia, P.; Raulerson, E. K.; Coleman, D.; Gerke, C. S.; Mangolini, L.; Tang, M. L.; Roberts, S. T. Achieving Spin-Triplet Exciton Transfer between Silicon and Molecular Acceptors for Photon Upconversion. *Nat. Chem.* **2020**, *12* (2), 137–144. https://doi.org/10.1038/s41557-019-0385-8.

(4) Kroupa, D. M.; Vörös, M.; Brawand, N. P.; McNichols, B. W.; Miller, E. M.; Gu, J.; Nozik, A. J.; Sellinger, A.; Galli, G.; Beard, M. C. Tuning Colloidal Quantum Dot Band Edge Positions through Solution-Phase Surface Chemistry Modification. *Nat Commun* **2017**, *8* (1), 15257. https://doi.org/10.1038/ncomms15257.

(5) Weidman, M. C.; Beck, M. E.; Hoffman, R. S.; Prins, F.; Tisdale, W. A. Monodisperse, Air-Stable PbS Nanocrystals *via* Precursor Stoichiometry Control. *ACS Nano* **2014**, *8* (6), 6363–6371. https://doi.org/10.1021/nn5018654.

(6) Hines, M. A.; Scholes, G. D. Colloidal PbS Nanocrystals with Size-Tunable Near-Infrared Emission: Observation of Post-Synthesis Self-Narrowing of the Particle Size Distribution. *Advanced Materials* **2003**, *15* (21), 1844–1849. https://doi.org/10.1002/adma.200305395.

(7) Kessler, M. L.; Starr, H. E.; Knauf, R. R.; Rountree, K. J.; Dempsey, J. L. Exchange Equilibria of Carboxylate-Terminated Ligands at PbS Nanocrystal Surfaces. *Physical Chemistry Chemical Physics* **2018**, *20* (36), 23649–23655. https://doi.org/10.1039/C8CP04275F.

(8) Hedström, S.; Chaudhuri, S.; La Porte, N. T.; Rudshteyn, B.; Martinez, J. F.; Wasielewski, M. R.; Batista, V. S. Thousandfold Enhancement of Photoreduction Lifetime in Re(Bpy)(CO) $_3$ via Spin-Dependent Electron Transfer from a Perylenediimide Radical Anion Donor. *J. Am. Chem. Soc.* **2017**, *139* (46), 16466–16469. https://doi.org/10.1021/jacs.7b09438.

(9) Anderson, N. C.; Hendricks, M. P.; Choi, J. J.; Owen, J. S. Ligand Exchange and the Stoichiometry of Metal Chalcogenide Nanocrystals: Spectroscopic Observation of Facile Metal-Carboxylate Displacement and Binding. *Journal of the American Chemical Society* **2013**, *135* (49), 18536–18548. https://doi.org/10.1021/ja4086758.

(10) Bronstein, N. D.; Martinez, M. S.; Kroupa, D. M.; Vörös, M.; Lu, H.; Brawand, N. P.; Nozik, A. J.; Sellinger, A.; Galli, G.; Beard, M. C. Designing Janus Ligand Shells on PbS Quantum Dots Using Ligand–Ligand Cooperativity. *ACS Nano* **2019**, *13* (4), 3839–3846. https://doi.org/10.1021/acsnano.9b00191.